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Environmental and In Situ SEM/TEM

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TEM holder for *in situ* transfer

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The conditions under which samples are studied using *in situ* techniques are in general not the real operando conditions, because these conditions are too harsh. Instead a set of conditions compatible with the instrumentation for characterization are used, like sample geometry, temperature, gas environment etc.

Environmental transmission electron microscopy (ETEM) studies are usually performed using conventional sample holders in a dedicated ETEM [1] or in a traditional TEM by use of a dedicated high-pressure cell sample holder [2]. In both cases, the setup defines the conditions regarding gas, pressure and temperature, which usually are far from the operando conditions of e.g. heterogeneous catalysis. Our efforts focus on bridging these gaps by establishing *in situ* sample transfer between complementary measurement techniques.

ETEM depends on complementary experiments and characterization techniques. Normally, this is done in parallel with experiments separated in time and space [3] or mimicking a reactor bed by changing the feed gas composition according to reactivity and conversion measured in dedicated catalyst set-ups [4]. Furthermore, dedicated transfer holders have been used to transfer catalyst samples between reactor set-ups and TEM at room temperature in inert atmosphere [5]. To take the full advantage of complementary *in situ* techniques, transfer under reactions conditions is essential.

This study introduces the *in situ* transfer concept by use of a dedicated TEM transfer holder that is able to enclose the sample in a gaseous environment at temperatures up to approx. 900°C. By oxidation and reduction experiments of Cu nanoparticles (NP's) it is shown possible to keep reaction conditions outside the microscope.

Figure 1 (A) and (B) shows CAD drawings of the TEM holder tip in open and closed configuration, respectively. The combined MEMS sample grid and micro heater [6] is mounted inside an aluminium compartment. The MEMS based heater ensures fast response and reach of temperature equilibrium. Figure 1 (C) shows a high resolution TEM (HRTEM) micrograph acquired at 150°C in 1.2 mbar H_2 of a 4 nm Cu particle. Figure 2 shows electron energy loss spectrum (EELS), TEM micrograph, and electron diffraction pattern (ED) of Cu nanoparticles (NPs) reduced in 1.2 mbar H_2 at 280°C. The acquisition was performed at 150°C in 1.2 mbar H_2. EELS and ED confirms the metallic state of the Cu NP.

A significant difference is observed between a reduced sample exposed to 150°C in a closed holder configuration with 1.2 mbar H_2 for 15 minutes (Fig. 3) outside the microscope and a reduced sample exposed to 150°C in an open holder configuration i.e. ambient condition for 15 minutes (Fig. 4). The *in situ* transfer sample kept at 150°C in 1.2 mbar H_2 during the simulated transfer shows same EELS, TEM, and ED behaviour as the reduced sample shown in Fig. 2, whereas the sample that experienced 150°C at ambient conditions shows significant changes. EELS shows characteristic "white lines" in the Cu signal that indicates an increased oxidation state of Cu. The TEM micrograph shows clear morphology changes and core-shell structures. This implies that the sample is not fully oxidized and correlates well with ED showing rings that resembles both Cu and Cu_2O.

The study shows that it is possible to keep reaction conditions outside the microscope and thereby opens up for the possibility to do complimentary *in situ* experiments of the exact same sample without changing the sample condition during transfer.

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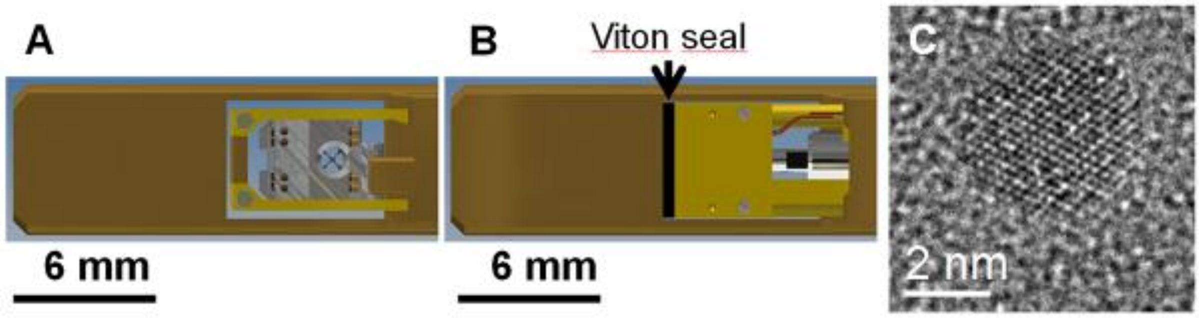

Figure 1. Tip of TEM *In situ* transfer holder in open (A) and closed (B) configuration. HRTEM image acquired at 150°C in 1.2 mbar H_2 of a 4 nm Cu particle.

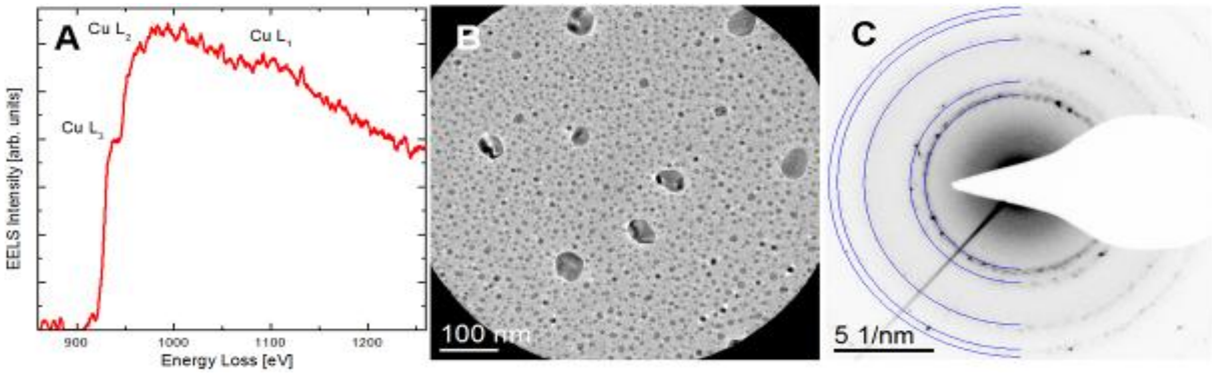

Figure 2. EELS spectrum (A), TEM image (B), and ED (C) acquired at 150°C in 1.2 mbar H_2. The sample was reduced in 1.2 mbar H_2 at 280°C prior to acquisition. The blue rings in (C) represent the theoretical reflections from metallic Cu.

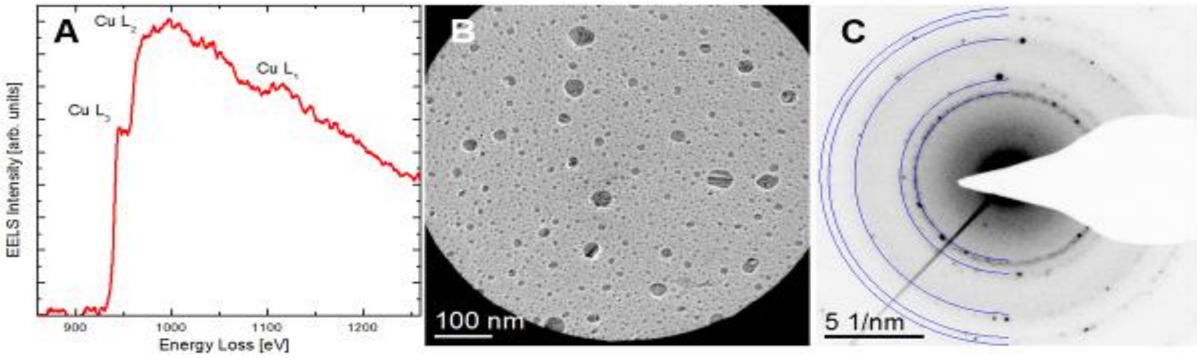

Figure 3. EELS spectrum (A), TEM image (B), and ED (C) acquired at 150°C in 1.2 mbar H_2. The sample was kept at 150°C in ambient conditions with holder in closed configuration. The transfer compartment was closed inside the ETEM in 1.2 mbar H_2. The blue rings in (C) represent the theoretical reflections from metallic Cu.

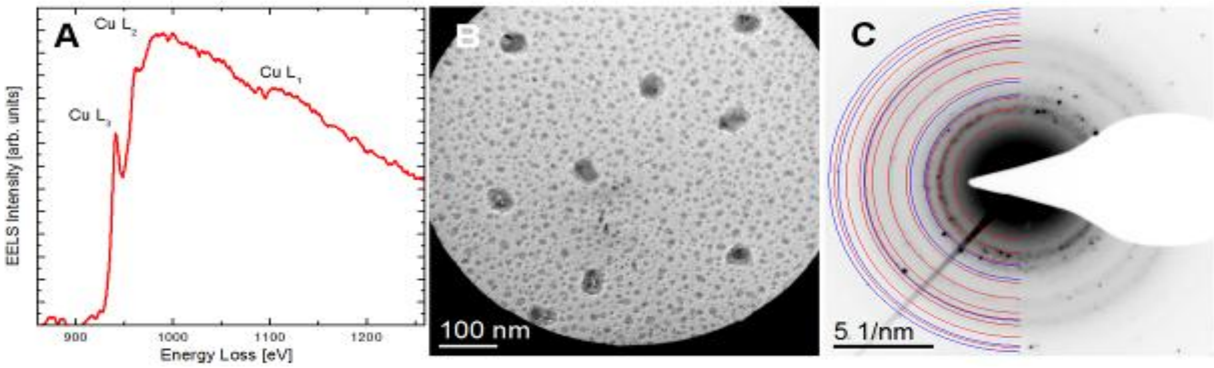

Figure 4. EELS spectrum (A), TEM image (B), and ED (C) acquired at 10^{-5} mbar. The sample was kept at 150°C in ambient conditions with holder in open configuration. The blue and red rings in (C) represent the theoretical reflections from metallic Cu and oxide Cu_2O, respectively.